ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 6, Issue 8 , August 2019

Some Aspects of Retrofit of Natural Gas Cleaning Processes

N.S. Salidjanova, Sh.O. Shomirzaev,G.G. Nabiev, S.R.Valiev

Doctor of Technical Sciences, Head of the Joint-Stock Company «Uzbekistan oil and gas planning and research institute», Tashkent, Uzbekistan,
Head of the department of engineering, supervision LLC «Muborekgas processing plant», Muborek, Uzbekistan,
Doctor of Philosophy, Main specialist Joint-Stock Company «Uzbekistan oil and gas planning and research institute», Tashkent, Uzbekistan,
Master's degree, Research assistant Joint-Stock Company «Uzbekistan oil and gas planning and research institute», Tashkent, Uzbekistan.

ABSTRACT: Now for cleaning of gas from hydrogen sulfide and carbon dioxide the regenerative technology with application of chemisorbents is used. The basic advantages of this technology-high and reliable degree of gas cleaning irrespective of partial pressure of hydrogen sulfide and carbonic acid, low viscosity of water absorbing solutions, low absorption of hydrocarbons that guarantees high quality of the sour gases, raw material for sulfur production . From chemisorbents most widely alkanolamines are applied. Use of chemical solvents is based on chemical reaction between chemisorbent and sour components. The maximum absorbing ability of water solutions of chemical absorbents is limited by stoichiometry. The most known ethanolamines, used in processes of gas cleaning from H_2S and CO_2, are diethanolamine (DEA) and metyldiethanolamine (MDEA).

KEYWORDS: natural gas, technology of cleaning, amines, absorbents

I. INTRODUCTION

Retrofit and optimization problems of the procedure of natural gas processing for the purpose of ensuring production efficiency and quality of feed gas cleaning inLLC«Mubareksky gas-processing plant» (MGPP), being the oldest gas-processing enterprise of the oil and gas branch of Uzbekistan, are undoubtedly, actual. It is necessary to notice that in process of increase in terms of gas condensate fields development the removal of highly-mineralized formation water, containing mechanical impurities from bottomhole zone, increases. This phenomenon leads to increase in moisture content of the produced hydrocarbon gas containing aggressive impurities of corrosion-active sulfur containing compounds (hydrogen sulfide, carbon bisulfide, mercaptans, sulfides, disulfides, etc.), and toughening of the requirements, producible to processes «drainage-regeneration». Thereupon research of the by-products allocated from absorbers, definition of influence of saturated and regenerated amine solutions, and antifoam on formation of by-products [1-3] are of interest.

II. LITERATURE SURVEY

For cleaning of natural gas from H_2S and CO_2 and mercaptans various processes are applied which can be broken into following groups [3,4]:
• Processes of physical absorption where extraction of sour components happens at the expense of their solubility in organic absorbers;
• Chemisorption processes based on chemical interaction H_2S and CO_2 with active part of absorbent;
• The combined processes using simultaneously chemical and physical absorbers;
• The oxidation processes based on irreversible transformation of absorbed hydrogen sulfide in sulfur;
• Adsorption processes based on extraction of gas components by solid absorbers-adsorbents (molecular sieves, activated coals, etc.).
To the absorbents used in the industry, such requirements are produced, as high absorbing ability, selectivity, low viscosity, unlack and untoxicity [4,5].
Now for cleaning of gas from hydrogen sulfide and carbon dioxide the regenerative technology with application of chemisorbents is used. The basic advantages of this technology-high and reliable degree of gas cleaning irrespective of partial pressure of hydrogen sulfide and carbonic acid, low viscosity of water absorbing solutions, low absorption of

hydrocarbons that guarantees high quality of the sour gases, raw material for sulfur production. From chemisorbents most widely alkanolamines are applied. Use of chemical solvents is based on chemical reaction between chemisorbent and sour components. The maximum absorbing ability of water solutions of chemical absorbents is limited by stoichiometry. The most known ethanolamines, used in processes of gas cleaning from H_2S and CO_2, are diethanolamine (DEA) and metyldiethanolamine (MDEA) [4]. Use DEA is especially expedient when initial gas along with H_2S and CO_2 contains COS and CS_2. For selective extraction H_2S in the presence of CO_2 tertiary amine - MDEA [4,5] is used, as a basis of researches.

III. EXPERIMENTAL RESULTS

For experiment performance at MGPP following probes have been selected:

1 - saturated solution MDEA (shop 2, block 8);
2 - regenerated solution MDEA (shop 2, block 8);
3 - saturated solution MDEA (shop 4, block 13);
4 - regenerated solution MDEA (shop 4, the block 13);
5 - antifoam of mark Penta- 480;
6 - by-product from an absorber (like plaster);
7 - by-product from an absorber (foamed).

In table 1 basic characteristic of tested probes of amine are presented.

Apparently from table 1, (probe 4) regenerated solution has high density though its concentration is less that, probably, is caused by presence of mechanical impurities and degradation products of amine solutions in the regenerated solution.

Table 1. Characteristics of tested probes of amine solutions

№ of probes	pH at 20^0C	Concentration, %	GOST 3900 Density, $\rho 4^{20}$ °C, g/cm^3	GOST 3900 Content of mechanic impurities, %	GOST 6370 Content of total sulfur, % (ISO 8754 ASTMD 4294)	Corrosion ability (ISO9001:2008)
1	11	20,03	1,054	0,17	0,2546	not bear
2	11	20,38	1,050	0,18	0,2037	not bear
3	11	21,28	1,054	0,19	0,1527	not bear
4	11	21,81	1,022	0,11	0,1059	not bear

In table 2 results of definition foaming ability of analyzed solutions MDEA are presented.

From data in table 2 it is visible that addition even of insignificant quantity of antifoam effectively influences on foaming ability of solutions MDEA with formation of the unstable large-cellular foam instantly destroyed.

For studying of absorption properties the scheme has been chosen whereas initial (basic) criterion of estimation of absorbents properties their selectivity in relation to carbon dioxide is accepted. Features of such scheme:

• Use of 100%- carbonic gas excludes the influence on gas phase resistance and quantity of the absorbed carbonic gas is defined only by properties of absorber (at other equal conditions);

• A reactionary surface (a spiral in absorber by which absorbent flows down) is rather small to provide selectivity and sufficient to carry out interaction CO_2 and absorber;

• As a measure of selectivity of absorbent, rate of absorption of carbonic gas per unit of sorbent volume of the same molarity compared to the standard is accepted;

Table 2. Foaming capacity of saturated and regenerated solutions MDEA

Index	Probe 1	Probe 2	Probe 3	Probe 4
Foam height, mm	7,0	7,3	7,8	8,0
Foam stability, c	1080	90	3270	285
With antifoam of mark Penta - 480				
Foam height, mm	0,5	0,3	0,5	0,2
Foam stability, c	1,0	< 1	< 1	< 1

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 6, Issue 8 , August 2019

Thus time of contact of identical doses of tested absorbers should be of one order. For quantitative estimation of selectivity H_2S in relation to CO_2: laboratory researches defined rate of absorption CO_2 by absorbent solution of definite molarity under the formula:

$$\omega = VCO_2/N \cdot \tau (cm^3/mol \cdot sec), \quad (1)$$

Where V - volume of absorbed CO_2,cm^3; N - quantity of reacted amine moles; τ- experience times
Thus it is considered - the above rate of absorption, the lower selectivity, and the selectivity evaluation only on absorption $C0_2$ is based on that rate of absorption H_2S by amine solutions is much more above.
In order to define rate of absorption CO_2 by laboratory installation, regenerated solutions MDEAwere used. Averaged results of the spent researches are presented in table 3.
Apparently from table 3, by the greatest selectivity possesses the regenerated solution MDEA tested as probe 4

Table 3. Definition of rate of absorption CO_2 (cm^3/mole ·sec) by regenerated MDEA solutions

Regenerated solutions MDEA	
Probe 2	Probe 4
3,39	2,25
3,37	2,31

Thus, based on spent researches it is possible to draw conclusions:
- Absorption rate of carbonic gas by regenerated solutions depends on concentration of a solution.
- Fall of concentration leads to fall absorption ability of solutions MDEA.

The analysis of impurities composition was spent under the scheme:
- Definition of sulfide sulfur;
- Iron definition;
- Sulfides definition;
- Definition of silicon oxides.

Analysis conducting on definition of physic and chemical parameters of antifoam Penta-480 has shown full conformity with TU 2229120-40245042-2007.
It is established that tested probe 6 is well soluble in all organic solvents, insoluble in water, and weak-soluble in acids and alkalis, i.e. the given sample of this probe represented by itself oil- component mixture. In this connection the furtheranalysis of the sample of the probe 6 was conducted under the scheme of oil research.

Table 4. Results of mass-spectrometer analysis

Index	Metals								
Concentration, mg/kg	Fe	Mn	Ti	Cr	Zn	Ni	Cu	V	W
	85000	870	1700	290	330	110	110	44	8

The probe of the given sample was processed by 40-multiple volume of light condensate. As a result asphaltenes in quantity of 32,024% were allocated. The remainder part of the sample was processed with the concentrated sulfuric acid (ρ-1,84 g/cm^3) for allocation of hydrocarbon compounds of paraffin order:
- Oxidized pitches yield - 25,7%;
- Oil yield - 43,8%, including paraffin - 4,12%;
- Mechanical impurities - 2,6%.

Thus, it is established that the sample of probe 6 represents the asphalt-gum-paraffin deposits containing mechanical impurities.
It is established that all investigated solvents extracted from the sample of probe 7, are sulfur containing compounds, and content of general sulfur fluctuates from 0,1% to 2,8%. The greatest quantity of general sulfur is recovered by polar solvent (chloroform) where its content reaches about 3%. It isnecessary to notice that the basic share here falls on polymeric part. The output of hydrocarbons not exceed 30 %.
As a result of conducting qualitative chemical reactions it is established that in probe 5, as well as in probe 7 silicon oxide is. The basic share of components in these tests falls on silicon-organic compounds. For confirmation of the data received by chemical method, studies of probes 5 and 7 by method IK-spectroscopy have been conducted. In IK-spectra identical strips of absorption are observed. So, in antifoam spectrum intensive strips of absorption -1018,18 $cm^{-1}$and 1095,44 cm^{-1} corresponding to stretching vibrations O-Si, and in a spectrum of the foamed sample a strip of absorption - 1017,94 cm^{-1} and 1090,99 $cm^{-1}$are observed. Strips of absorption in the field of 2963,04 cm^{-1} (probe 5) and

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 6, Issue 8 , August 2019

2963,18 cm^{-1} (probe 7) should be attributed, possibly, to communication fluctuations $(CH_3)_3SiO$. Presence of absorption strips in the field of 1446 cm^{-1}in a spectrum of probe 7 and weak strips in area from 500-700 cm^{-1}speaks about presence of sulfides in the probe. In antifoam a strip of absorption in the field of 1446 $cm^{-1}$is absent. Besides, in probe of antifoam 5 and7 strips of absorption 1261,24 cm^{-1}, 864,38 cm^{-1} and 1260,95 $cm^{-1}$and 870 cm^{-1} - are observed, accordingly, which should be attributed to symmetric deformation fluctuations Si CH_3.
It is necessary to notice also that in spectrum of antifoam there are the strips of absorption Si-O-CH_3 related to fluctuations - 2850,14 cm^{-1} and in probe of by-product -a strip of absorption 2851,54 cm^{-1}. In spectrum of antifoam in area-800,03 cm^{-1} an absorption strip can be attributed to dissymmetric valence fluctuations - SiOCO-CH_3, in a spectrum of by-product of probe 7 - 799,72 cm^{-1}.
In spectra the wide strip in the area of 3402,14 cm^{-1}, and 3382,69 cm^{-1} is observed which can be attributed to O—H valence fluctuations, and also strip of absorption 1640,94 cm^{-1}, related, most likely, to water of crystallization. In solution of antifoam this strip is more intensive compared to the probe 7 where it is presented in the form of an arm. Besides, in a spectrum less intensive strips of absorption, typical to siloxanes are observed. It is necessary to notice also that in a spectrum of probe 7 the intensive strip 1651,02 $cm^{-1}$is observed which, possibly, may be attributed to aliphatic amines . The weak strip of absorption - 2127,26 cm^{-1}, related to products of thermal decomposition of amines is observed.
On the basis of the spent IK-researches it is established that the solid foamed product the sample of probe 7 represents basically organic-silicone compounds of siloxane type, also as well as antifoam (probe 5).
Studies of mechanical impurities of the sample of probe 7 on metals content were spent by a method of plasma spectroscopy on device ISR-MS (mass spectrometer of the induction-connected plasma+) AT 7500. Results of the analysis are presented in table 4.
Apparently from the data presented in table 4, the basic share of yield falls on iron and its compounds - 48,6%. Presence in mechanical impurities of the high content of iron testifies passing of corrosion processes. Presence in slime such elements as manganese nickel, copper, chrome, is possible to explain by steel corrosion processes from which these elements have got to mechanical impurities.

IV. CONCLUSION AND FUTURE WORK

Thus, based on the spent chemical, mass spectral and IK-spectroscopic researches it is established that the by-product (the sample of probe 7) is formed as result of aggregate chemical reactions of antifoam, hydrocarbons, thermal amines decomposition and sulfur containing compounds. The given process is catalyzed, possibly, by metals, formed as a result ofcorrosion processes which can be caused by incomplete absorption of amine solutions of sour gases. The sample of probe 6 represents asphalt-gum-paraffin deposits.
Results of the spent researches cause conducting of the following measures on optimization of existing technology «drainage-regeneration»:
• Strictly to supervise process of gas treatment and concentration of solutions MDEA depending on quality (humidity, content of mech. impurities, H_2S, CO_2, etc.) of the incoming to the enterprise raw stock;
• To place additional filters for more effective continuous filtration of amine working solutions;
• To reconsider, proceeding from real situation, the schedule of periodic washing and cleaning of devices, and the equipment from possible slimes;
• To strengthen corrosive situation control in system treatment-drainage-regeneration.
The developed measures will allow to optimize rigid, according to existing technology, operating regime of the equipment of the enterprise, caused by influence of mechanical loadings, temperatures, contact interaction and influence of corrosive environments, and also use of considerable quantity of chemical reagents of various classes (according to existing technology) that will provide strengthening of industrial safety of processes of natural gas processing.

REFERENCES

[1] Afanasev A.I., Stryuchkov V. M, etc. Technology of processing ofsulfuric natural gas//Moscow .Nedra, ,pages l52, 1993.
[2] Bekirov T.M., Lanchakovв. A. Technology of processing of gas and condensate // LLC «Bowels-business centre» Moscow, pages 596, 1999.
[3] Agaevв. A. Struggle against foaming in process of amine cleaning of natural gas//M. VNIIE Gazprom, (Rev. inform. Sulfurs. Cleaning and processing of gas and gas condensate, issue 3) pages 33, 1979.
[4] AgaevG.A.Tabatabai AM., KasimovaPM Research in the field of selection effective defoamants for amine processes of natural gas cleaning. M. VNIIEgazprom, pages 38, 1976.
[5] Gilyazetdinov LP. Foaming and defoaming in processes of gas processing. Moscow. VNIIEgazprom, pages 48, 1984 (Rev.inform.Sulfurs. Treatment and processing of gas and gas condensate, issue. 5).

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 6, Issue 8 , August 2019

AUTHOR'S BIOGRAPHY

SalidjanovaNafisaSagdullaevna – Doctor of Technical Sciences, Head of the Laboratory of anticorrosive protection of the Joint-Stock Company «Uzbekistan oil and gas planning and research institute». She is a Authoress more than 150 publications, including 14 patents, two mono-graphs. Expert in industrial safetyin oil and gas sector.

ShomirzaevShuhratOmanovich - Head of the department of engineering, supervision LLC «Muborekgas processing plant», Muborek, Uzbekistan. Area of scientific interests- anticorrosive protection of gaz-processing enterprises equipment, in particular – insulating materials. The expert of 2 nd level UZK and VICK of the international standard EN – 473. He is Author more than 40 publications, including 2 patents.

NabievGairatjonGanievich - Doctor of Philosophy, Main specialist of the Laboratory of anticorrosive protection of theJoint-Stock Company «Uzbekistan oil and gas planning and research institute».He is Author more than 80 publications, including 2 patents.

ValievSaidjonRustamovich - Master's degree, Rese-arch assistantof the Laboratory of anticorrosive protectionof the Joint-Stock Company «Uzbekistan oil and gas planning and research institute».He is Author more than 20 publications, including 1 patent. Expert in indestructible control in oil and gas sector.